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Title: Bonding and Distribution as a Function of Depth in Pu and U Forensic Samples HSHQDC-15-X-B0004 – LANL

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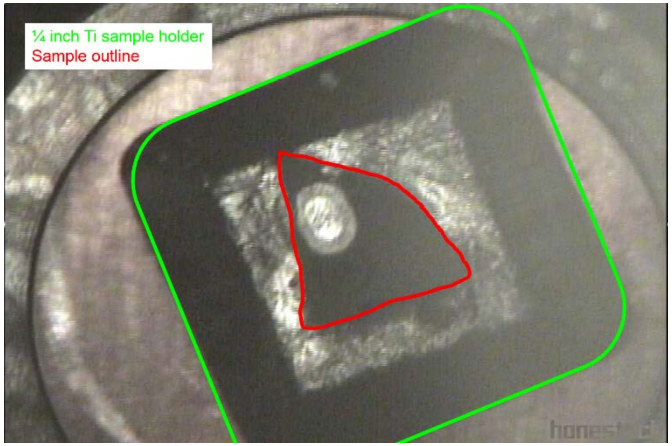
Bonding and Distribution as a Function of Depth in Pu and U Forensic Samples
HSHQDC-15-X-B0004 – LANL

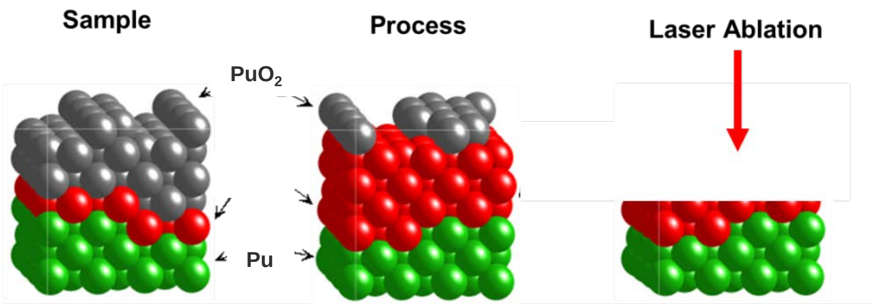
John Joyce , Kevin Graham, Brian Scott, Paul Tobash, Laura Wolfsberg, Jason Lashley-LANL

Los Alamos National Laboratory
work for Department of Homeland Security

July 27, 2017
Oak Ridge National Laboratory

Overview





Combine XPS at different energies & collection angles with laser ablation to map local bonding and impurities. Using high surface sensitivity with laser ablation provides insight into local process environment.

Los Alamos National Laboratory

People

Total employees: 11,200, including approximately:

•Los Alamos National Security, LLC: 7,200

•Students: 1,600

•Post doctoral researchers: 350

Budget, FY 2016

Approx. $2.45 billion

Facilities

More than 1,000 individual buildings, 8.2 million feet^2 under roof (13 nuclear facilities), 43 miles^2

Nuclear Forensics – Areas of Interest

- **Can divide forensic interest into 3 areas.**
  - **Time domain** (get a sample, when was it processed – isotopes, ratios)
  - **Bulk characterization** (elements in a sample – maybe some bonding)
    - photons, very high energy electrons
  - **Surface/interface characterization** (elements, bonding, distribution w depth)
    - electrons, ions, laser ablation for depth probe – Storage forms show head gas
    - How much environmentally oxidized Pu/U needs to be milled away to reach the underlying metal/bulk Pu/U can be realized with XPS & laser ablation.
    - The rate that impurities diminish from the surface region also gives information on the processing and storage environment of samples.

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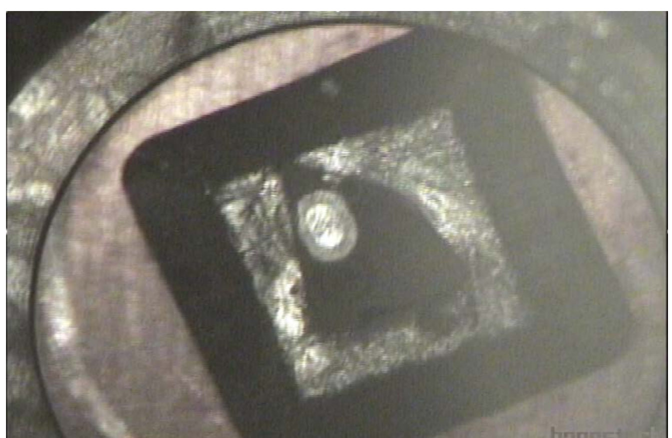
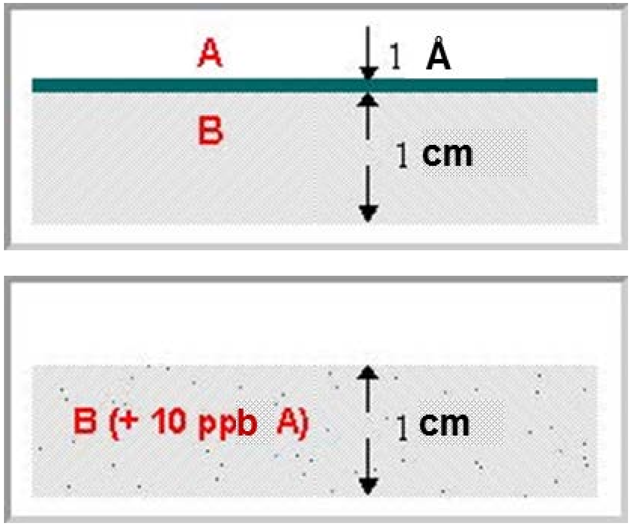


Surface/Bulk Probes - Sensitivity



Sensitivity of XPS is generally about 0.5 - 1% for many elements, possible to get down to 0.1% in very favorable circumstances. If impurities or contaminants are localized near a surface it is easy to detect with XPS.

Sub-monolayer surface element = 10 ppb in a 1 cm sample. (F, C, Ga, Fe common in some actinides)

A voxel is the 3D analog of a pixel, it is a volume unit. In additive manufacturing, voxels can have unity dimensions. In XPS the volume that is probed can be considered a voxel, but it is very asymmetric. Our instrument has an area limit of 300 μm diameter min to 3x3 mm max. The vertical probe dimension is ~ 2 nm to 8 nm. We can take an XPS voxel at any point in the ablation process but it would be very labor intensive to deconstruct microns of material depth without gaps.

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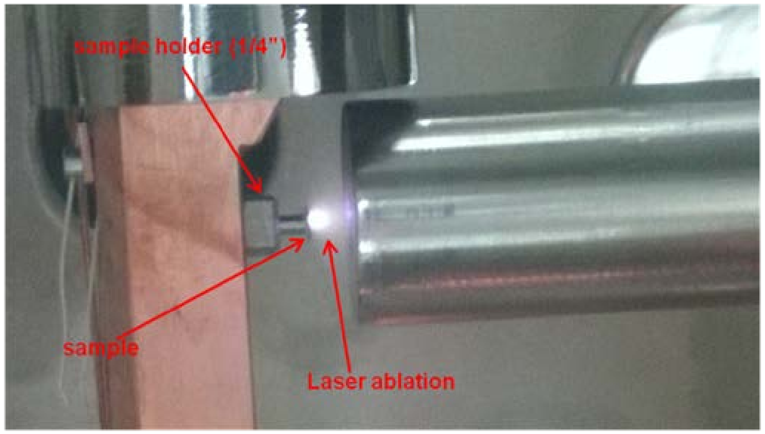
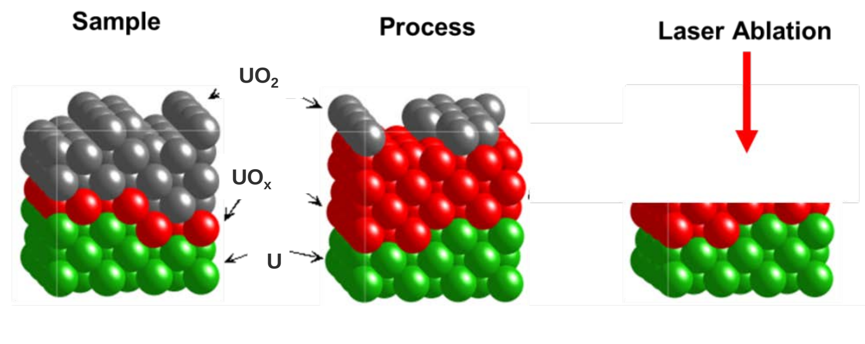
Laser Ablation – Probing Surface to Bulk

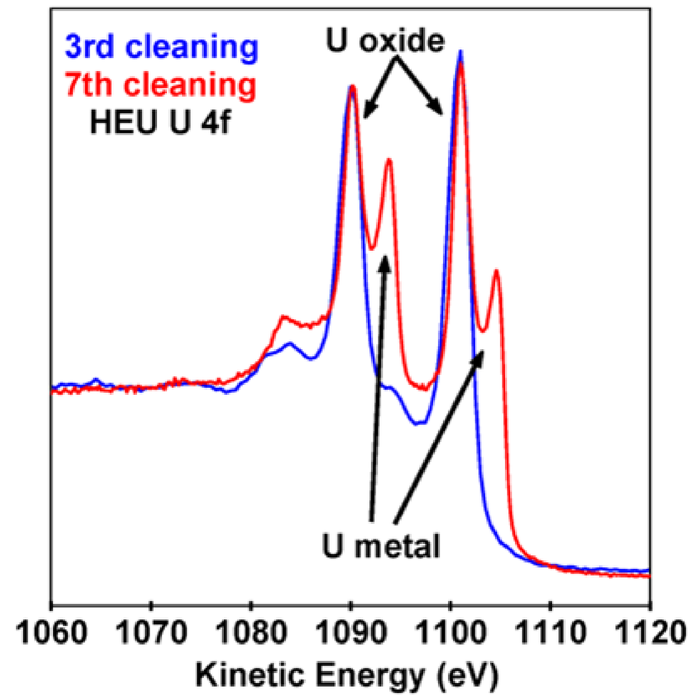




With XPS we can identify the elements in a sample, we can also identify how an element is bonded to neighboring atoms by chemical shifts.

With laser ablation we can remove atomic layers and identify elements and bonding as a function of sample depth.

We receive samples from other programs (LEP, surveillance) and characterization from other programs (LDRD). We also leverage with other DHS interests.



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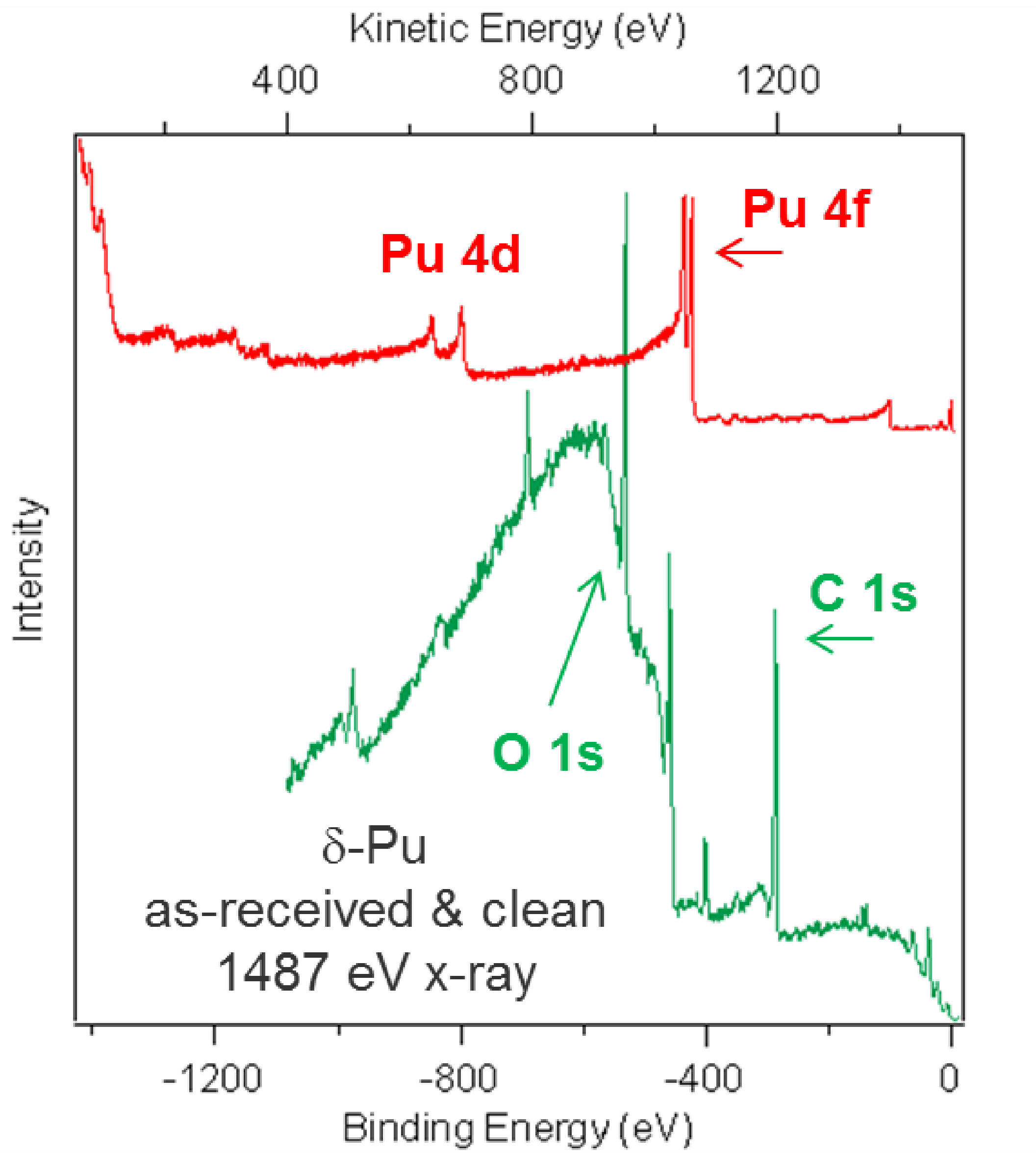
XPS – Probing Surface to Bulk

- Using Laser ablation we can mill away outer (surface) layers of any sample.
- The model of oxidized Pu (or U) being milled away down to the underlying metal is realized in the Pu data on the right with green (as-received) and red (cleaned with ablation).
- The rate that various light elements diminish from the surface also gives potential information on processing history of samples.



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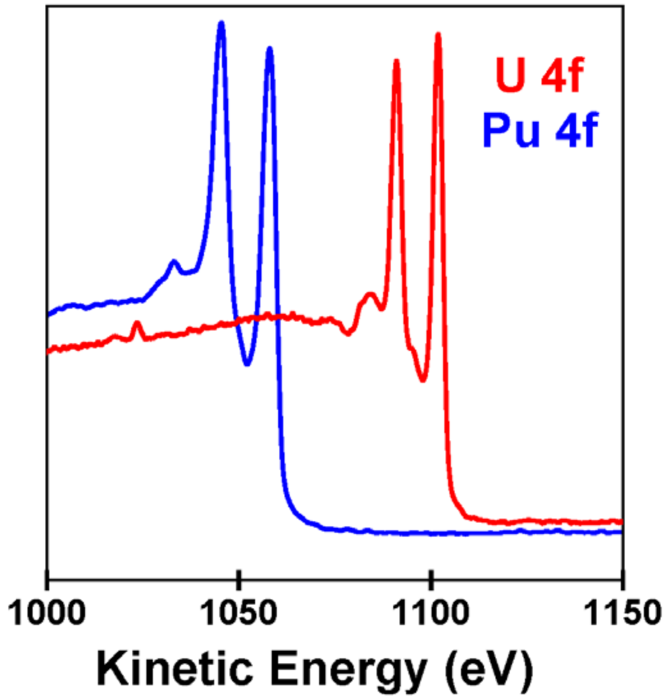
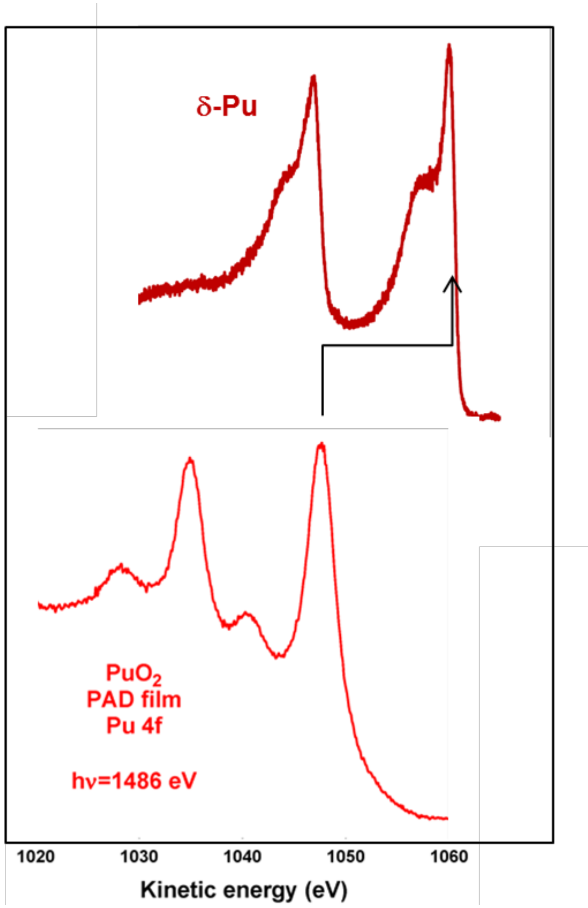
XPS – Elements & Local Bonding



Left: XPS data showing the 4f core-levels of Pu and U. Binding energy difference is over 50 eV, easy to observe. **Right:** XPS data showing Pu 4f levels for δ-Pu and PuO_2. Under favorable conditions we can see phase differences



- We can measure elements from Li to Pu using XPS (H & He at lower energies if needed). We can also distinguish Pu-O from Pu-Pu bonding.

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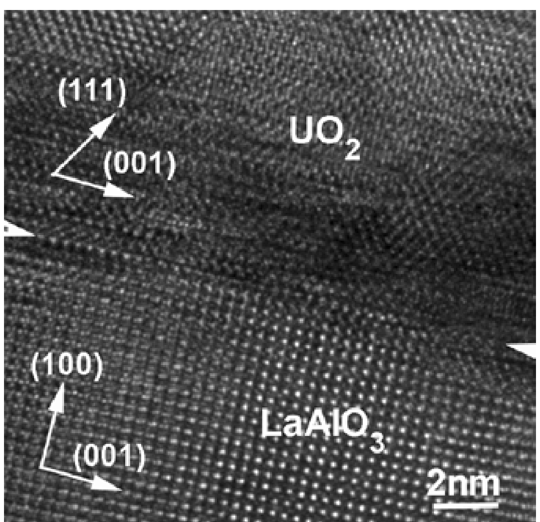
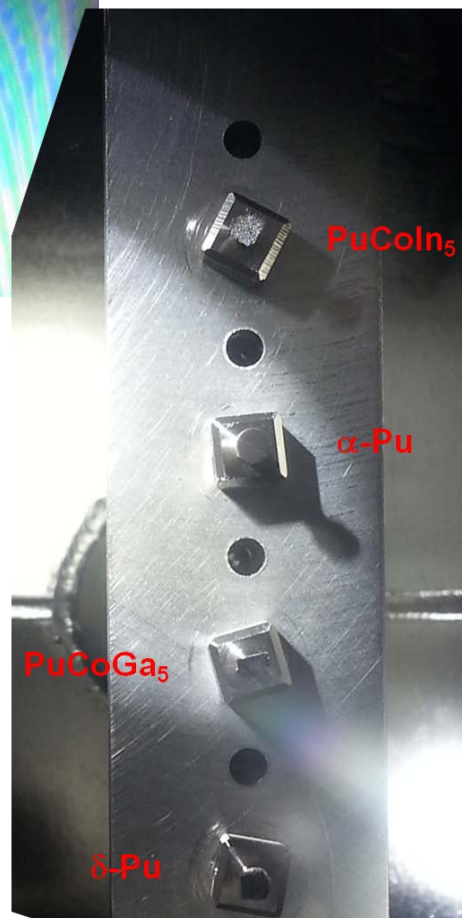
Nuclear Forensics Samples & Ablation

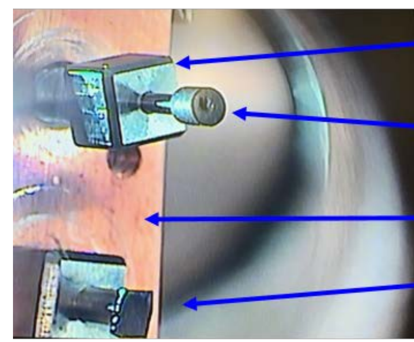
Brian Scott, Laura Wolfsberg- PAD PuO_2, UO_2, CeO_2, HEU foil
Paul Tobash, Pu/U/Ce metal
Jason Lashley- bulk U, UO_2

PuO_2 PAD mounted on Ti sample holder, screwed into Cu cryostat

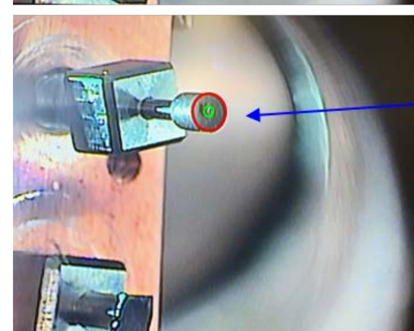


4 Pu samples in prep chamber





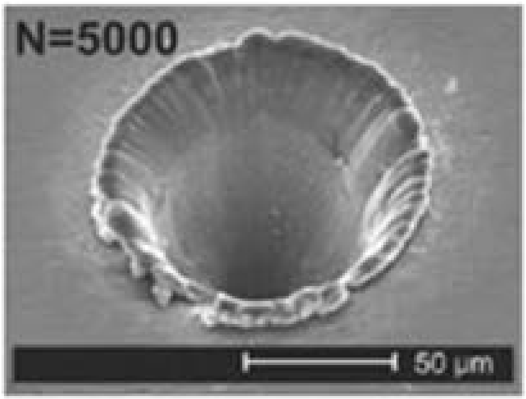
Ti sample holder
Ce on U metal
Cu cryostat
Pu metal



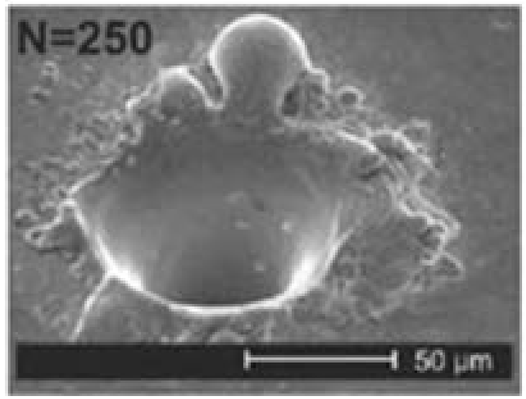
U metal
Ce metal

Nuclear Forensics – Laser Cleaning

ps pulse



ns pulse



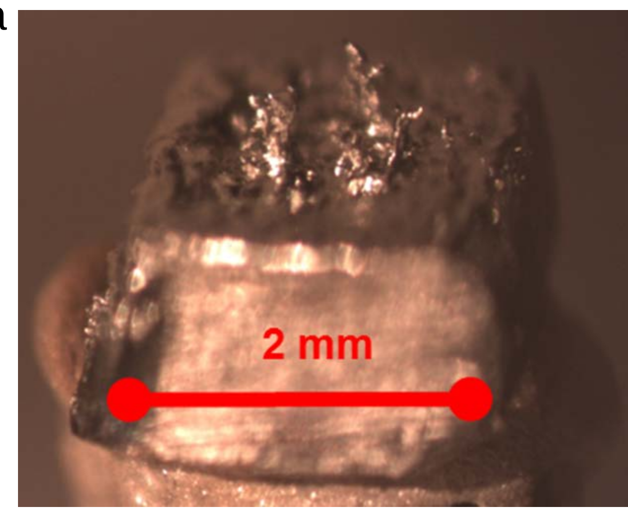
Laser ablation on SS targets: The ns pulses are dominated by thermal (melting) while ps pulse are non-thermal (explosion).
From Pulsed Laser Ablation of Solids – Basics, Theory and Applications, Springer-Verlag, 2014

ps laser pulses preserve sample integrity (compared to ns laser or ion sputtering)

Minimal heat limits diffusion of impurities

Material disruption limited to focus area

ps laser cleaning on U metal foil



ns YAG laser cleaning on delta Pu

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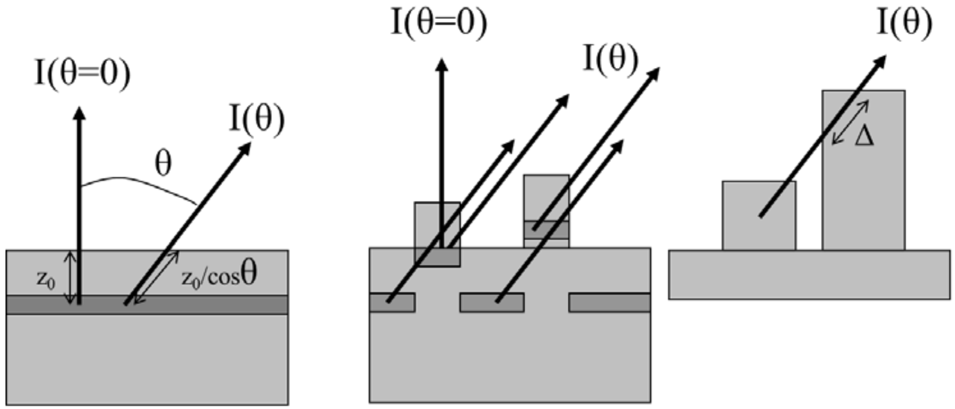
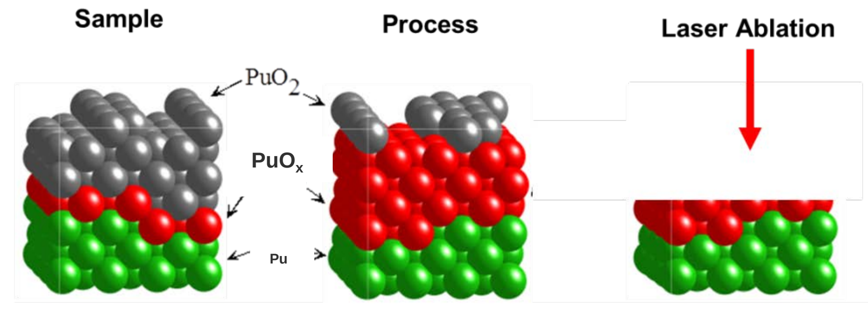
XPS – Probe Depth - Morphology



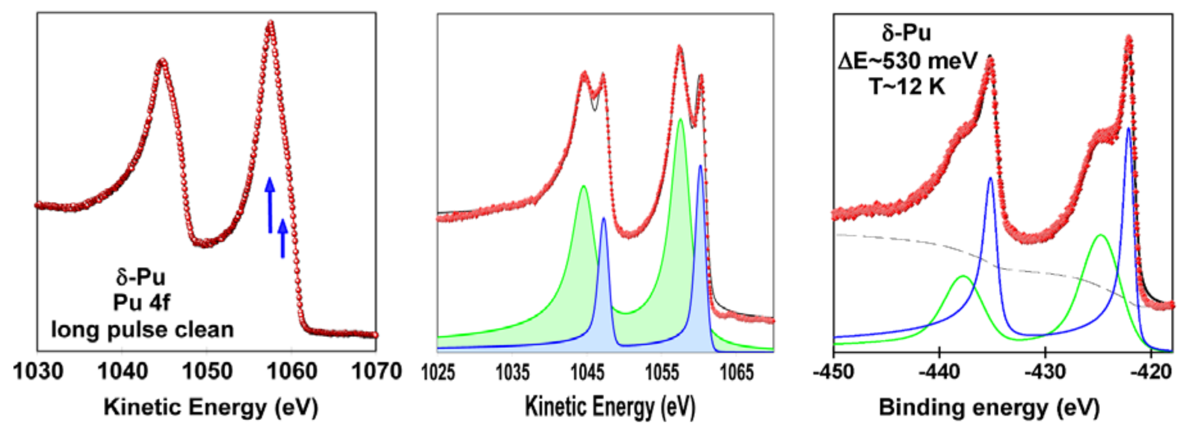
Flat surface

Rough surface



Above: schematic of different surface structures. We use 3 XPS methods (takeoff angles, Tougaard, 2 photon energies) to distinguish rough from flat surfaces. Using 1 or 2 methods might leave ambiguity in assessment. Using all 3 methods allows separation of surface roughness from element distribution in the probe depth.

Below: XPS data for Pu 4f levels (red dots) shown with lineshape fitting to identify two sets of peaks and a background function. Fitting quantifies analysis parameters;



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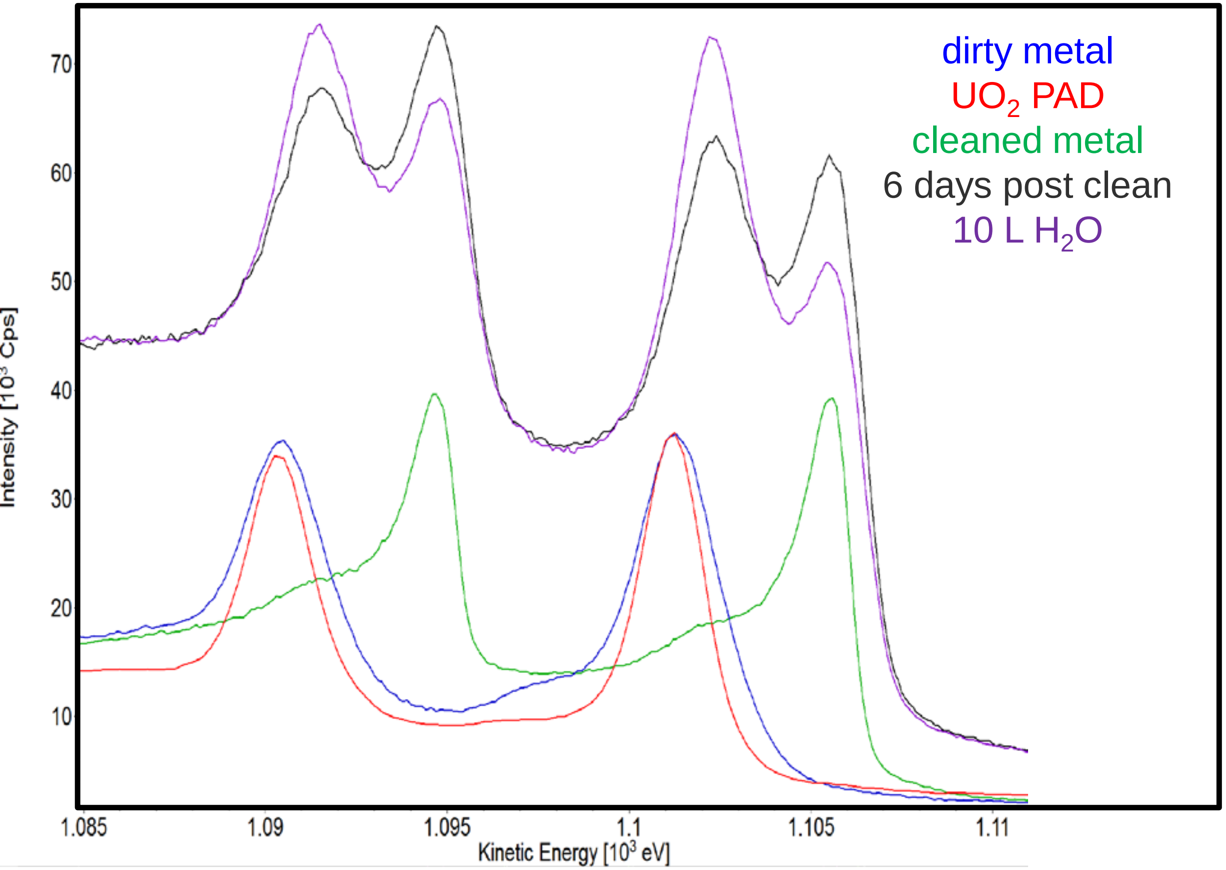
XPS 4f Cores – Bonding – Local Sites

U metal, oxide and dosing – U 4f core-levels



Details of the U 4f core-level showing large differences in local bonding configurations including clean and dirty metal, high quality UO_2 film and vacuum contaminated metal as well as controlled, dosed metal.

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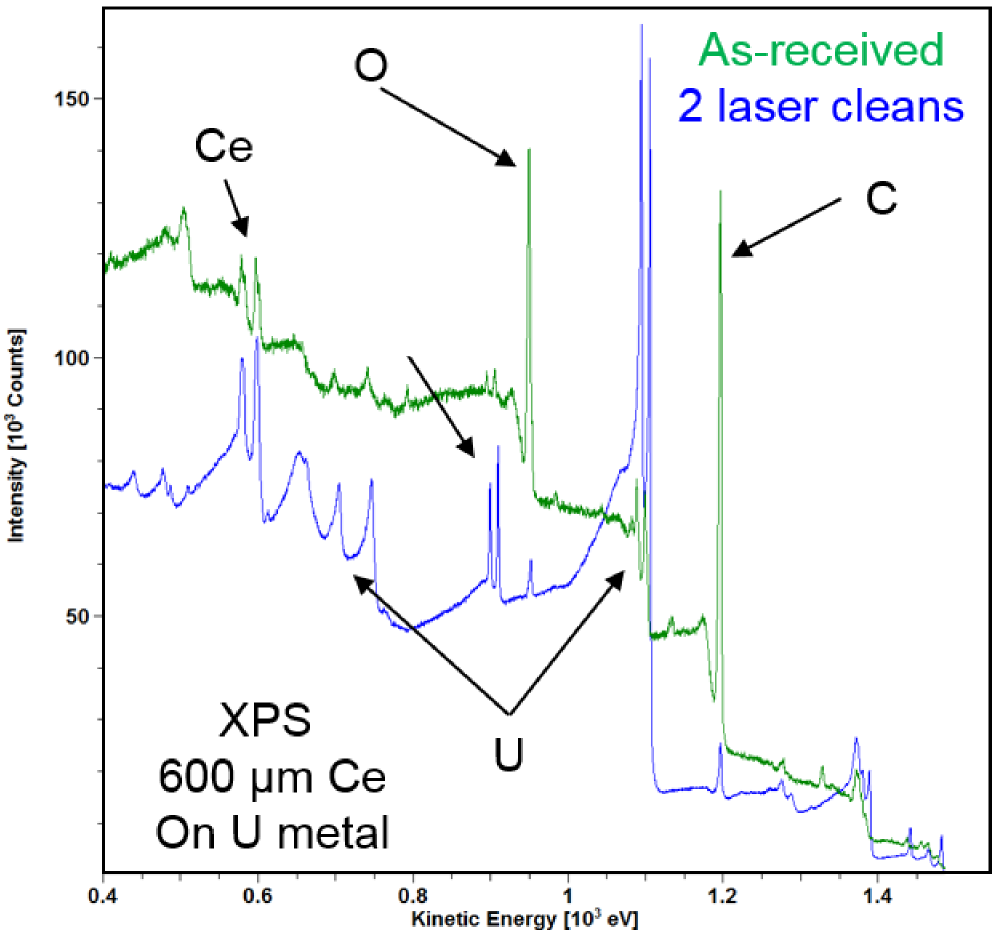
XPS Complex Metals & Depth Profile



A mechanically joined metal sample of Ce on U metal. The XPS broad spectrum shows Ce and U as well as O and C. The ratios of Ce and U to C and O change between the as-received sample and the sample after laser ablation. One also observes a change in the Ce core-level lineshape between the cleaned and as-received sample.

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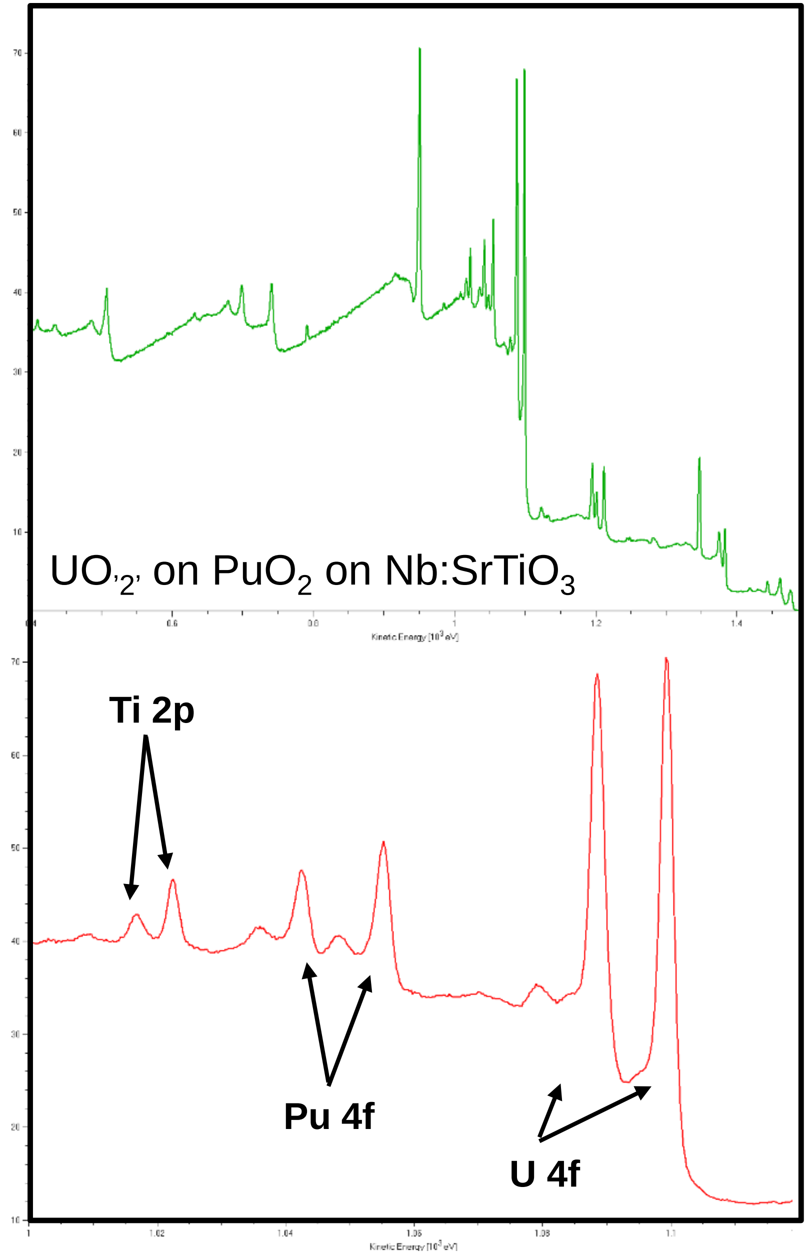
Complex Oxides – UO_x on PuO_2

As we move to more realistic sample environments or forensic samples, mixed actinides will challenge our signature capability. On the right we show thin film UO_x on PuO_2 on a $SrTiO_3$ substrate. The detailed XPS spectrum shows substrate, underlying PuO_2 and UO_2 peaks all within the probe depth of the XPS.



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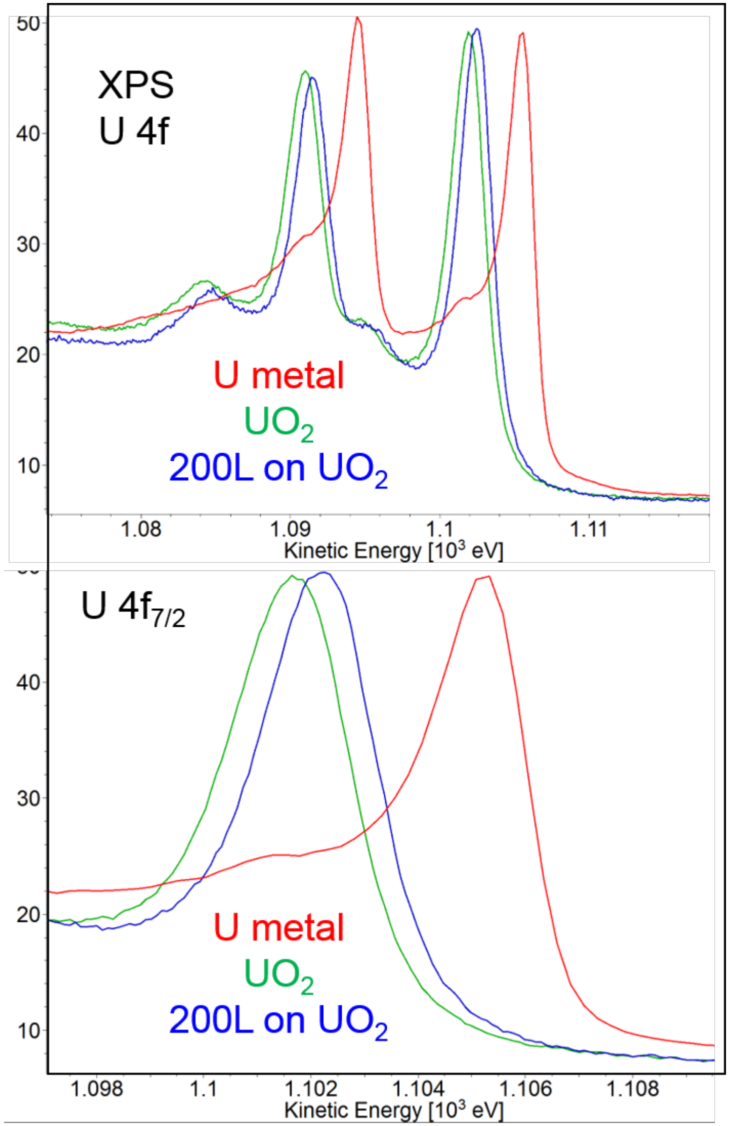
XPS – Impurities in Metal & Oxides

Controlled dosing of H on UO_2 sample. The energy difference between the metal and the dioxide is 2.7 eV. The shift away from the UO_2 peak position for the U 4*f* level is 500 meV when exposed to 200 L of H_2 gas. The binding energy of UH_3 is very close to that of U metal. Hydrogen is a common contaminant in Pu and U due to processing of the material to a metal.



Summary

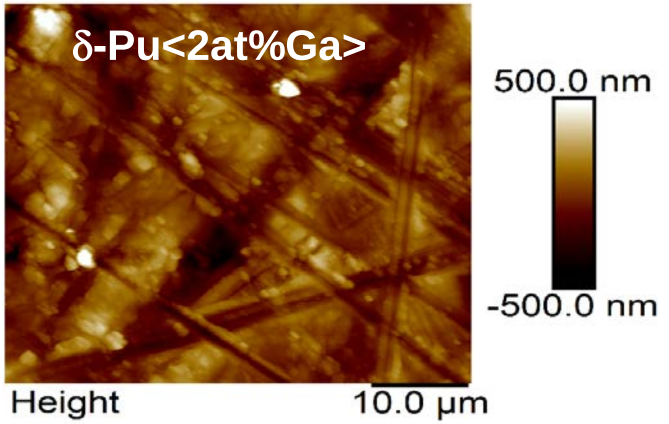
Advancing new capability in nuclear forensics using:

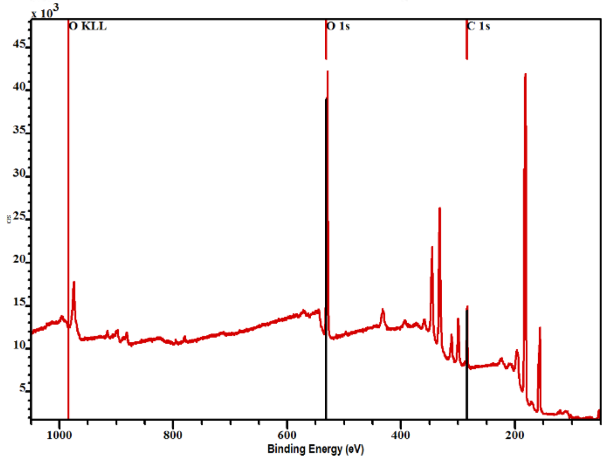
1) state-of-the-art x-ray photoelectron spectroscopy (Pu & U lineshapes, C, O, F and many other impurities identified for process history assessment).
2) advanced picosecond laser with advantages over standard YAGs (no melting, little mobility of impurities, changes localized to beam area).
3) cutting edge sample synthesis (PAD for Pu/U/Ce oxides, single X-tal samples & unique sources)
4) a combination of analysis techniques providing maximum information from samples with minimum uncertainty.

➢This capability for nuclear forensics has nanoscale probe depth and the XPS capability to distinguish local bonding environments as well as impurities localized to specific regions of the sample depth. We probe on the surface, near the surface and deep into the bulk via laser ablation.

Surface Science at LANL for Nuclear Forensics

- **Future Directions:** New opportunities in Pu/An Forensics enhanced capability with new equipment funded by other sponsors.
- Atomic Force Microscopy (AFM), 10 μm XPS (μXPS), Secondary Ion Mass Spectroscopy (SIMS) – all Pu and U capable and in one location.
- The synergy of actinide research people and surface spectroscopy equipment will provide an actinide (Pu/U) science capability that is unique in the world. The existing XPS/Laser Ablation capability is moving to co-locate with these new spectroscopies.





XPS, SIMS, Laser Ablation, μXPS, Auger, Imaging

T. Venhaus, J. Joyce, D. Moore, S. Hernandez, D. Olive, K. Graham (MST-16)

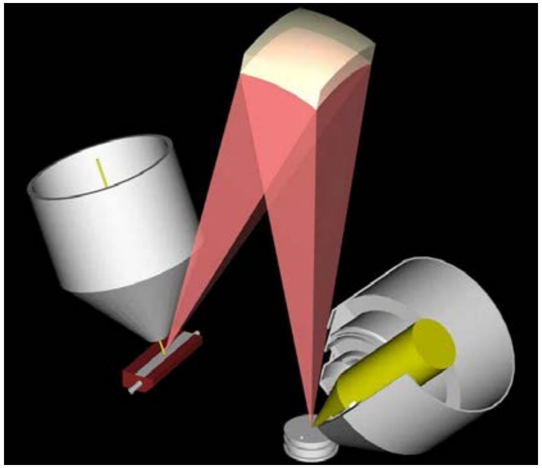
AFM (also STM/STS)

M.F. Beaux, M. Santiago Cordoba, N. Leon Brito, and I.O. Usov (MST-7)

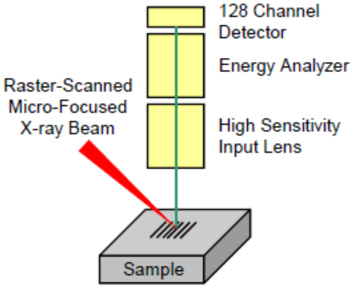
Los Alamos National Laboratory – Materials Science & Technology Division

2017: XPS- AES - SEI

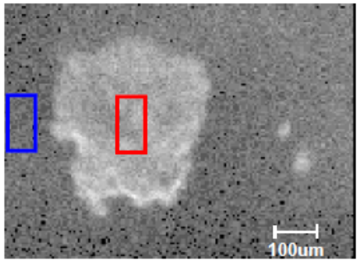
- XPS: **lateral resolution to 10µm**
- Auger Electron Spectroscopy (AES)
- Secondary Electron Imaging (SEI -SEM) – **100 nm resolution**
- Ion Sputter Depth profiling
- Laser Ablation Depth Profiling ⇨ end CY2017 (proposed)
- Anticipate Pu capability Fall 2017
- Acceptance testing complete
- Currently operating non-transuranic



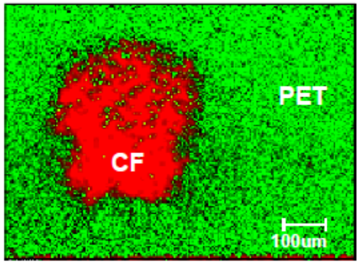
VersaProbe III
Scanning XPS Microprobe



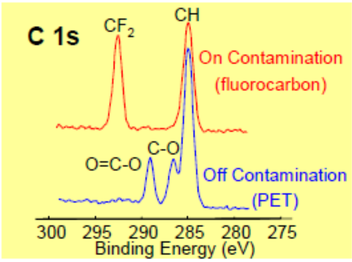
Secondary Electron Imaging
of Contamination on a Polymer Film
Not Visible with an Optical Microscope



C 1s Chemical State Maps



Micro-Area Spectroscopy



LANL

Pu Time-of-Flight SIMS

SIMS: Sample bombarded with high energy ions, secondary ions mass analyzed

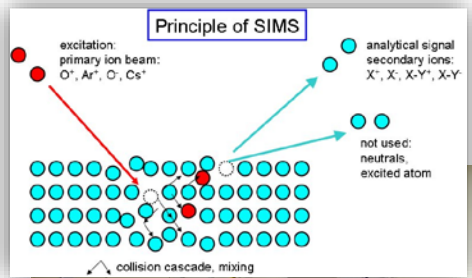
Technique sensitive to all isotopes (including Pu & U isotope distribution), from hydrogen to Pu and beyond (molecules/clusters)

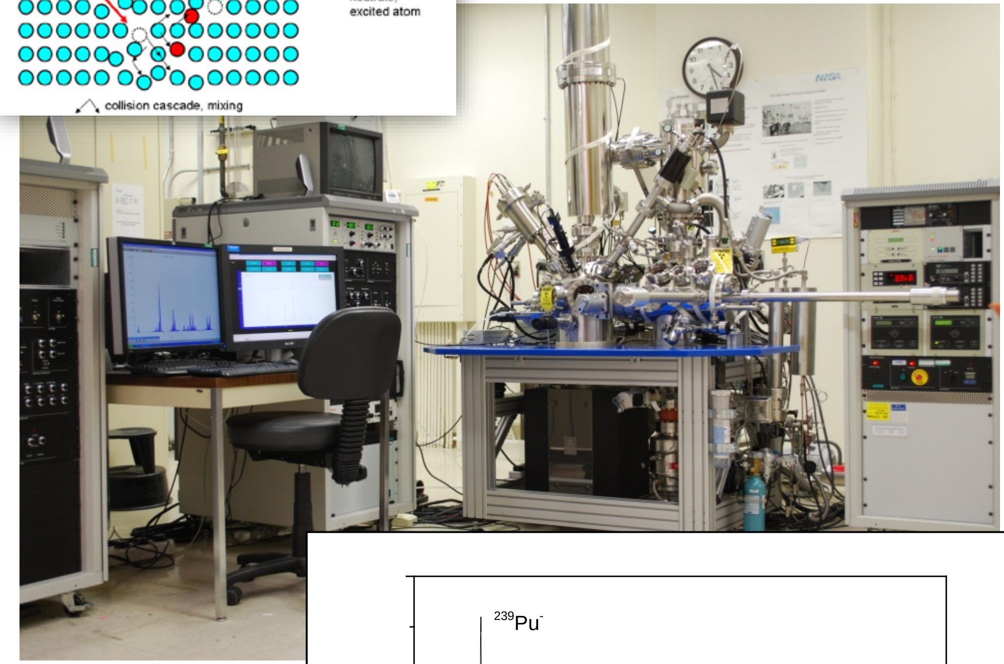
Dynamic range of 10^6

Mapping capabilities with spatial **resolution of < 1µm**

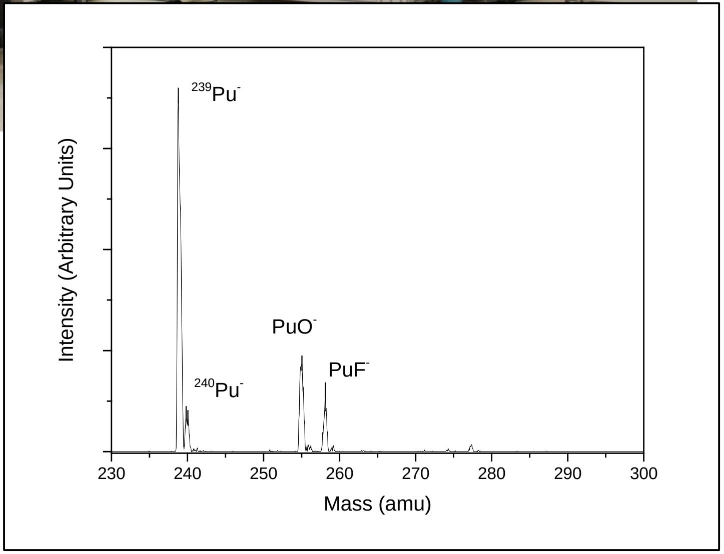
Can perform isotopically labeled exposures (e.g. $^{18}O_2$, CD_4) for "tracer" experiments and surface exchange reactions

System fitted with reaction cell for *in situ* Pu hydriding





The Kore ToF-SIMS at TFF

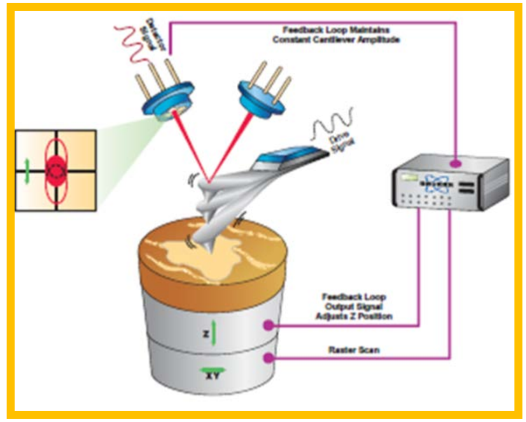


Pu spectrum from the ToF-SIMS

Pu Atomic Force Microscopy (AFM)

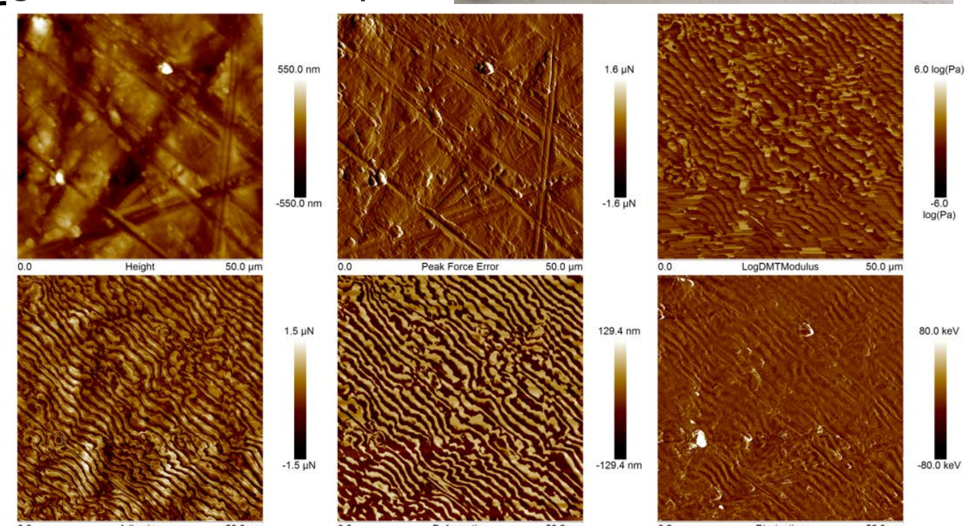
Bruker Multimode AFM:

- Height & Amplitude Modes
  - ✓ 3D morphology
- Phase Contrast Mode
  - ✓ qualitative mapping of surface mechanical and chemical properties
- Peak Force Mode
  - ✓ quantitative mapping of surface mechanical properties
  - ✓ quantitative measurements of friction coefficients
- Lateral Force Mode
  - ✓ qualitative mapping of friction coefficients
- Broad range of other imaging modes for additional tip-sample interactions (surface potential, magnetic force, electrical conductivity, etc.)



Glove box housed Pu AFM

Images from δ-Pu coupon



These images could be processed through MAMA software

Future Plans

- In the next year we will use laser ablation and XPS to investigate complex samples of Pu and U in metal and oxide forms. Sample development will include Ce metal and oxides. We will further explore opportunity for ‘off-site’ forensic samples.

- Year three samples will have Pu and U materials in intimate contact to exercise spectroscopic capabilities to quantify and characterize overlapping actinide signatures.

- These year three studies will compare against the year two work now concluding where Pu and U (oxides and metals) were investigated in layered or mechanically joined samples.

Broader opportunities for nuclear forensics beyond next year could include AFM, SIMS, μXPS, SEM (SEI) with an emphasis on near surface to bulk transition regions providing insight into foreign process/storage and manufacturing capabilities.